

Atomic Hydrogen as a Reducing Agent

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Atomic hydrogen is a powerful chemical reducing agent. It may be used to perform reductions at lower temperatures than those achieved in molecular hydrogen, and since it is electrically neutral it is not subject to shielding effects. Because of the contradictory results reported in the literature, an investigation was undertaken to determine optimum ways to produce and transfer atomic species. It is concluded that electrodeless discharge is the most reliable way of production, and that, although Teflon and phosphoric acid coated glass have very low catalytic activities toward recombination, Pyrex and quartz are satisfactory container materials. Reduction temperatures in both molecular and atomic hydrogen were established for a variety of oxides, and the latter were found to be substantially lower. Finally, the advantages and limitations of atomic hydrogen as a reducing agent are considered.

1. INTRODUCTION

The removal of surface oxides is an important step in the manufacture of electron devices. The objective of this process is usually to facilitate the wetting of solid surfaces by molten metals or to improve some electrical properties of the device by changing the surface properties of certain components. Oxide-free surfaces can be obtained by wet chemical treatments, by bombardment with accelerated particles or by reduction in a gaseous ambient. Each of these processes exhibits certain limitations. Liquid reagents leave residues and require additional cleaning, electron or ion bombardment is vulnerable to shielding effects, and the high temperatures necessary for gaseous reduction restrict its application on most assembled electron devices. A powerful gaseous reducing agent capable of removing oxygen at relatively low temperatures combines the virtues of all these methods.¹ A study was undertaken, therefore, with such a reagent, atomic hydrogen, to establish the feasibility of its use. The following discussion gives our findings on the following three questions: (1) how to produce and transfer atomic species, (2) how much decrease in reduction temperature can be expected compared

with those observed in molecular hydrogen, and (3) what are the limitations and advantages of using atomic hydrogen in device processing?

II. PRODUCTION AND TRANSFER OF ATOMIC HYDROGEN

To study reduction in atomic hydrogen, a source of atoms and a way to transfer them to the oxide surface must be established. There are several methods known to dissociate molecular hydrogen (ultraviolet radiation, thermal or electrical energies, etc.). The data in the literature, however, are contradictory to the extent that we found it necessary to evaluate them for our purposes.

Dissociation of molecular hydrogen on hot tungsten filaments was reported in 1911;² experimental conditions have been well established,³ and the method has recently been employed in absorption studies.^{4,5} Our experiments, however, showed it impractical for reduction purposes. The water vapor evolved during reduction oxidizes the tungsten filament, deteriorating the wire and contaminating the system with evaporated tungsten oxide.

Contamination is the major disadvantage of the electrical discharge method first described by Wood.⁶ The sputtering of the electrodes gradually contaminates the walls of the apparatus and, by increasing their catalytic activity, reduces the transfer of atoms to the probe. Cooling the electrodes by compressed air delays wall poisoning only by several hours. Similar observations were reported by Linnett and Marsden⁷ for an oxygen discharge. Many previous investigations using Wood discharges neglected this effect, suggesting that their results should be treated with caution.

The theory of the electrodeless discharge was outlined by Thomson⁸ in 1928, and an efficient way to produce high concentrations of atomic hydrogen was described by Jennings and Linnett.⁹ This is the method we have essentially adopted. A schematic diagram of the apparatus is shown in Fig. 1. The quartz or Pyrex discharge tube, 50 mm in diameter, was surrounded by a gold-plated copper electrostatic screen to restrain the plasma from spreading beyond the coil. The screen was connected to ground and a distance of 3–4 mm was maintained between the screen and the discharge coil with the help of a quartz-tube spacer. The discharge was established with a variable-frequency (5–16 mc), 5-kw Lepel high-frequency generator, and the exciting coil consisted of eight turns of 6-mm copper tubing. The temperature of the tube was kept below 300°C by a jet of compressed air. The apparatus was connected to a mechanical vacuum pump, and a steady-state pressure of 200 μ was maintained by means of an adjustable leak. Pressure was measured

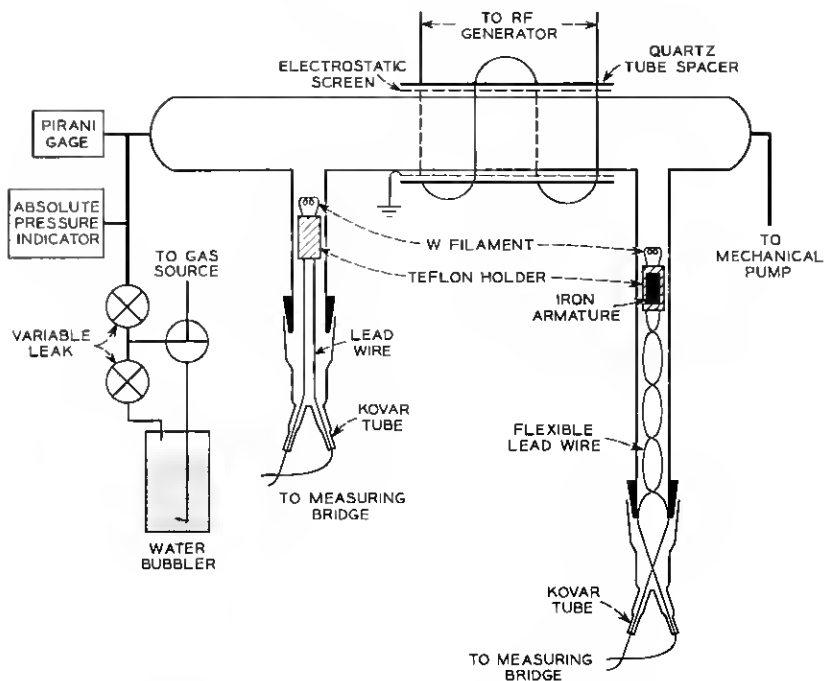


Fig. 1—Schematic diagram of the electrodeless discharge apparatus.

with a conventional Pirani gauge and a Wallace and Tiernan absolute pressure indicator. Since all the experiments were carried out in the side tubes, the flow of atoms in the reduction zone was purely diffusional.

The concentration of the atomic hydrogen was measured calorimetrically by a method similar to that described by Wood and Wise.¹⁰ Since the recombination on tungsten has been reported to change at lower temperatures due to surface poisoning,¹¹ the probe temperature was always kept above 150°C by a constant-voltage dc source (energy w_1). The heat evolved by recombination of hydrogen atoms increased the filament temperature; this was measured by supplying equivalent energy, w_2 , from the dc source after the discharge was terminated. The energy difference, $w_2 - w_1 = \Delta w$, is directly proportional to the number of atoms recombining on the probe. The side arms contained identical filaments, one of them serving only to check the stability of the atomic hydrogen concentration in the discharge tube. Considering the high concentration of atoms obtained, the reproducibility of the atomic level from one experiment to another and the stability of the

atomic hydrogen concentration during individual runs, the electrodeless discharge proved to be superior among the three methods tested.

III. THE TRANSFER OF ATOMIC HYDROGEN

The high reactivity of atomic hydrogen imposes serious difficulties in transportation and optimum utilization. Walls of low catalytic activity are needed to prevent recombination on the wall of the apparatus before reaction with the oxide. Many investigators have attempted to prepare surfaces of low catalytic activities and have offered explanations for the cause of this effect. Almost all have used, however, different experimental techniques and arrived at contradictory conclusions. The discrepancies are closely related to the question of whether or not hydrogen atoms can be produced in an electric discharge from dry gases.

Several investigators observed that the dissociation of hydrogen is greatly reduced⁶ or eliminated^{12,13} in the absence of water vapor. Coffin,¹⁴ on the other hand, found no appreciable decrease in the intensity of the Balmer lines in dry hydrogen. One explanation for the effect of water is that it poisons the catalytic activity of glass,^{3,6,15,16,18} however, two independent measurements using wet¹⁵ and dry¹⁹ hydrogen show practically identical catalytic activities. Smith¹⁵ obtained similar results after cleaning his apparatus with KOH, KHCrO₄, H₂SO₄, or HF, while others reported recombination coefficients different by three orders of magnitude for Pyrex rinsed in HNO₃¹⁹ and Pyrex rinsed in HF.²⁰ It can be concluded, therefore, that the role of water vapor in the production and recombination of atomic hydrogen is open for further clarification. Several attempts were made to poison glass and quartz surfaces by coating with phosphoric acid,^{3,15-17} with a mixture of dimethylchlorosilane and methyldichlorosilane ("Dry-film"),^{21,22} and more recently with Teflon.²³ No attempt was made, however, to evaluate the relative catalytic activities of the different surfaces.

In order to establish high concentration of atoms and walls of low catalytic activity, a series of experiments was carried out using both dry (water content <20 ppm) and wet hydrogen (by passing the gas through a water bubbler at 25°C) while changing the wall surface of the side arm. The inside diameter of the side arm was about 20 mm and the probe was positioned at a distance of $L/R = 10$, where L is the distance from the atom source and R is the radius of the tube. The stability of the atomic concentration of the source was checked continually by the probe in the second side arm. The results of all experiments are summarized in Table I. It is important to note that the heat evolved at the

TABLE I — THE ENERGY, Δw , RELEASED BY THE RECOMBINATION OF ATOMIC HYDROGEN ON THE TUNGSTEN FILAMENT AFTER DIFFUSING IN CYLINDERS OF DIFFERENT CATALYTIC ACTIVITIES. ($L/R = 10$, $\Delta w_0 = 150$ mw.)

Cylinder Wall	Δw (mw) in Dry Hydrogen	Δw (mw) in Wet Hydrogen
Teflon	86	85
Phosphorous coated Pyrex	80	81
Quartz rinsed with HNO_3	77	78
Pyrex rinsed with HNO_3	74	76
Pyrex rinsed with HF	75	74
Pyrex coated with dry-film	10-45	10-48

probe, Δw , is not a linear function of the catalytic activity of the wall^{24,25} and can be used only to establish a series of activities. Due to the limitations of Teflon toward heat treatment and the tedious cleaning procedures required with phosphoric acid coating,³ all the reduction studies were carried out in HNO_3 -rinsed Pyrex or quartz tubes with dry hydrogen.

IV. COMPARISON OF THE REDUCTION TEMPERATURES IN ATOMIC AND MOLECULAR HYDROGEN

The most important advantage of using atomic instead of molecular hydrogen is that a substantial decrease in the reduction temperature can be expected. An attempt was made, therefore, to compare the corresponding reduction temperatures in the two reducing atmospheres. Although some kinetic data for the reduction of metal oxides in hydrogen have been published before,²⁶ we have carried out reduction in both atmospheres to assure identical properties (impurity level, particle size, etc.) of the oxides. Since the reduction temperatures in atomic hydrogen were determined by observing the color changes of the oxides, it was also necessary to establish corresponding color-change temperatures in molecular hydrogen.

V. REDUCTION TEMPERATURES IN MOLECULAR HYDROGEN

Reduction in molecular hydrogen was carried out in the apparatus shown in Fig. 2. Reagent grade oxides in quantities producing about 3×10^{-3} moles of water upon reduction were placed into a quartz tube of 25 mm ID. The apparatus was flushed with dry nitrogen for several hours at temperatures ranging from 100° to 250°C. After cooling to room temperature the nitrogen flow was replaced by hydrogen (560

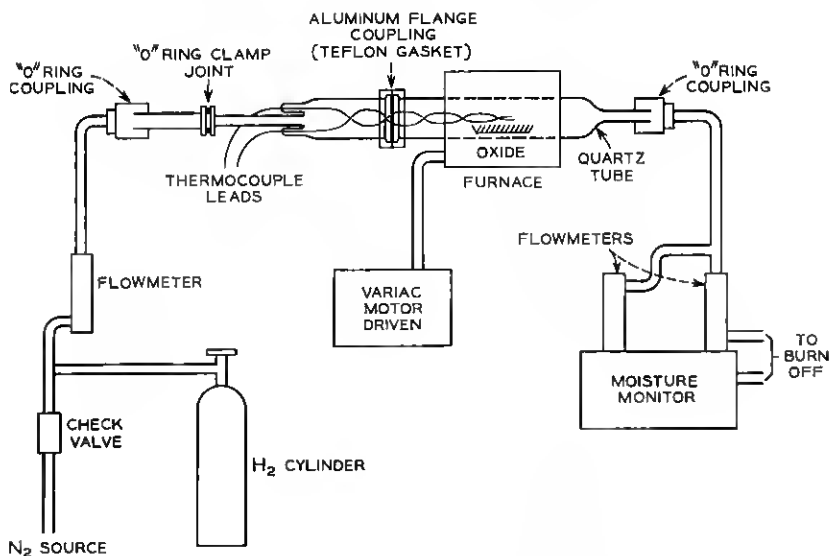


Fig. 2 — Hydrogen reduction apparatus.

cc/min) and the reduction cycle started, provided that the moisture content of the emerging gas was less than 10 ppm. The temperature of the tube furnace was raised at $5 \pm 1^\circ\text{C}/\text{min}$, and the moisture content of the gas was monitored continuously. The change in the moisture content as a function of temperature for the different oxides is shown in Figs. 3, 4, and 5. The temperatures at which color changes occurred were also noted. Reduction ranges and color change temperatures are summarized in Table II.

VI. REDUCTION TEMPERATURES IN ATOMIC HYDROGEN

Several investigators^{3,27} reduced metal oxides in atomic hydrogen; no attempt was made, however, to determine minimum reduction temperatures. The role of the heat of recombination on the reduction temperature was noted by Kroepelin and Vogel.³ They could reduce Cr_2O_3 only if the oxide particle contained catalytically active impurities and the heat of recombination raised the temperature above a critical point. The control of oxide temperatures imposes difficulties in atomic hydrogen. Since the recombination coefficient of Pyrex increases with increasing temperature,¹⁹ the apparatus wall cannot be heated along with the oxide without reducing atomic concentrations. Due to the

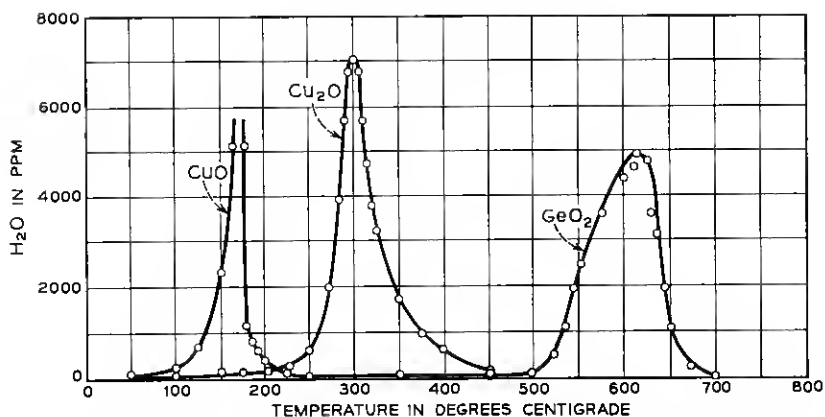


Fig. 3 — Reduction of CuO , Cu_2O , and GeO_2 in hydrogen: $[\text{O}_2]$ in oxides $= 1.5 \times 10^{-3}$ M; H_2 flow rate $= 560$ cc/min; temperature rise $\approx 5^\circ \text{C/min}$.

various catalytic activities and accommodation coefficients (the fraction of the heat of recombination transferred to the surface on which the recombination occurs) of the different oxides the heat of recombination yields different temperatures on each sample. Finally, the much higher catalytic activities of pure metals than those of the corresponding oxides result in a sudden temperature rise after reduction occurs. To overcome these difficulties, all oxide samples, 0.1 cm^2 in area and several

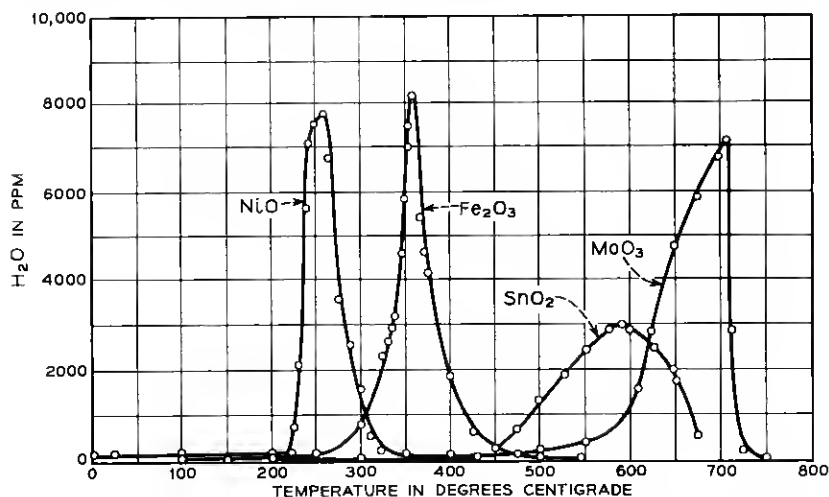


Fig. 4 — Reduction of NiO , Fe_2O_3 , SnO_2 , and MoO_3 in hydrogen: $[\text{O}_2]$ in oxides $= 1.5 \times 10^{-3}$ M; H_2 flow rate $= 560$ cc/min; temperature rise $\approx 5^\circ \text{C/min}$.

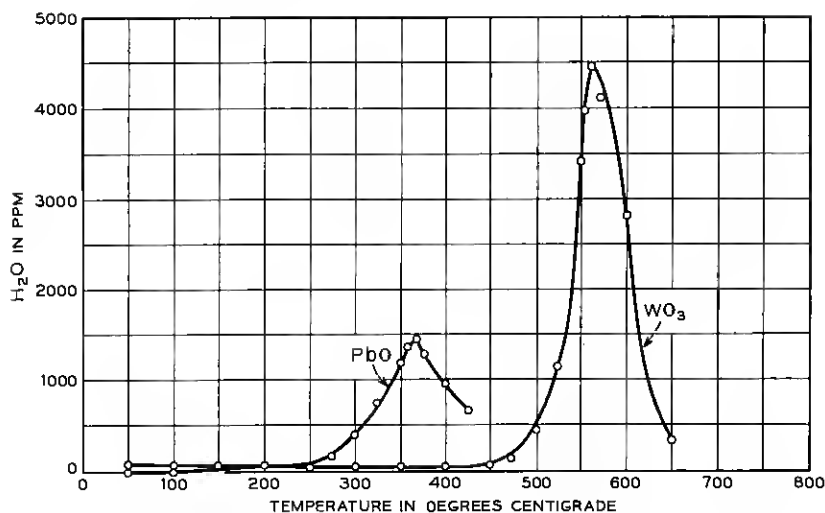


Fig. 5 — Reduction of PbO and WO₃ in hydrogen: $[O_2]$ in oxides = 1.5×10^{-3} M; H₂ flow rate = 560 cc/min; temperature rise $\approx 5^\circ$ /min.

microns thick, were placed on identical ceramic wafers. The wafers were 0.7 cm² in area and 2.0 mm thick, containing a hole for a thermocouple probe. The oxides were taken from the same lots supplying the material for the experiments in molecular hydrogen, and the reduction was continued until color changes — similar to those observed in H₂ — could be detected. The ceramic blocks were placed near to the entrance of the side arm and heated by the recombination of atoms on the block. The temperature rise was about 20°C/min and, due to the small areas involved, the presence of oxides did not influence this rate. The color

TABLE II — REDUCTION TEMPERATURES FOR DIFFERENT OXIDES IN MOLECULAR AND ATOMIC HYDROGEN (Temperature rise $5 \pm 1^\circ$ /min in H₂)

Oxide	Reduction Temp. in H ₂ (°C)	Color Change in H ₂ (°C)	Color Change in H (°C)
MoO ₃	500–725	610	43
GeO ₂	500–700	560	35
WO ₃	475–650	535	25
SnO ₂	400–675	490	100
Fe ₂ O ₃	250–500	310	40
PbO	225–475	300	25
Cu ₂ O	225–450	265	25
NiO	225–325	250	62
CuO	100–225	140	25

change temperatures with those obtained in molecular hydrogen are listed in Table II. Although all reduction temperatures are substantially lower in atomic hydrogen, no quantitative correlation could be established between the two sets of data.

VII. DISCUSSION

The most important advantage of using atomic hydrogen is lower reduction temperatures than those obtained in molecular hydrogen. This can be especially significant for stable oxides, not reducible in hydrogen below the melting point of the metal, such as Al_2O_3 , SiO_2 , etc. Removal of the oxide from aluminum inside an electrodeless discharge tube has been reported,¹⁰ and we have succeeded in removing SiO_2 films more than a micron thick from silicon slices.

The high reactivity of hydrogen atoms toward organic compounds makes it a potential remover of organic residues. Propane can be easily converted to methane at room temperatures²⁸ by the use of atomic hydrogen, and higher paraffins probably react in a similar manner. The formation of gaseous hydrocarbons was also reported on exposure of graphite to atomic hydrogen.²⁹

There are, however, several limitations to the use of atomic hydrogen. One is the difference in catalytic activities of different oxides, and that between metals and the corresponding oxides, those of the metals being much higher. If a complex system containing different materials were exposed to atomic hydrogen, it is likely that first the oxides with the largest catalytic activities would be reduced, and that the heat of recombination on the metals could melt some components before more stable oxides could be reduced. To determine whether a system can be exposed to certain atomic concentrations, a knowledge of the respective recombination and accommodation coefficients is required. While there is very little known about the latter quantity, the available data on the former are highly contradictory, as shown in Table III, and there are almost as many theories as authors for the property of the material determining its magnitude.

Another potential difficulty arises from the embrittlement of metals exposed to atomic hydrogen. Although no data are known about the solubility of atomic hydrogen in metals, it is reasonable to assume that it is greater than that of H_2 , especially for metals of group A (see Ref. 26, p. 518).

Finally, chemical interactions between atomic hydrogen and metals and metal oxides other than reduction should be considered. Partial reduction or hydride formation may occur with the formation of vola-

TABLE III — RELATIVE VALUES OF THE RECOMBINATION
COEFFICIENT OF ATOMIC HYDROGEN ON METALS
($\gamma_{Pt} = 1.00$)

Metal	Reference					
	27*	32	33	34	35	10
Pt	A	1.00	1.00		1.00	1.00
Co		0.98		1.00	0.72	
Pd	B		0.87		0.80	3.5
Ni		0.91		0.83	0.72	9.0
W	C			0.70		3.0
Fe	D	0.81		0.83	0.68	
Cr	E	0.71		0.60	0.64	
Ag	F		0.71		0.52	
Cu	G	0.74	0.66		0.76	5.5
Ti				0.68	0.40	19.0
Au					0.40	4.0
Al			0.47		2.5×10^{-2}	13.5

* A, B, C, ... : decreasing order of catalytic activities

tile products. Pietsch³⁰ formed compounds similar to lithium hydride by reacting atomic hydrogen with silver, beryllium, gallium, indium, and tantalum, while others³¹ formed volatile metal hydrides with germanium, tin, arsenic, antimony, and tellurium. In removing SiO₂ films, sometimes a black deposit on the discharge tube could be detected, the composition of which is not yet determined, and prolonged exposure of silicon to atomic hydrogen produced a pitted rough surface characteristic of gas phase etchings. It can hence be seen that the high reactivity of hydrogen can yield undesired effects such as the removal or damage of important surface areas and the contamination of certain parts of the system.

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